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On the high-pressure behavior of gobbinsite, the natural counterpart of the synthetic zeolite Na–P2

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ABSTRACT

An *in situ* high-pressure single-crystal X-ray diffraction study of gobbinsite, the natural counterpart of the synthetic zeolite Na–P2, was carried out up to 4.3 GPa. No evidence of amorphization was observed within pressure-range investigated. Using a non-penetrating *P*-medium, two changes of the elastic behavior occur: the first at 1.1–1.3 GPa and the second at 2.7–3.2 GPa. Birch-Murnaghan equations of state truncated to the second order were used to fit the experimental *P*–*V* data within the three *P*-ranges (i.e. 0.0001–1.1, 1.3–2.7 and 3.2–4.3 GPa), giving the following isothermal bulk moduli (K_{V0}): 46.3(9), 52(8) and 28(6) GPa, respectively. The unit-cell compression is significantly anisotropic. In response to the applied pressure, the 8-membered ring channel parallel to [100] undergoes a significant increase of ellipticity, whereas the channel parallel to [010] undergoes a shrinking towards a circular shape at $P \geqslant 1.3$ GPa. A partial re-organization of the H_2O sites occurs between 1.1 and 1.3 GPa, and new framework deformational modes onset at $P \geqslant 3.2$ GPa, coupled with a change in the coordination environment of the extraframework cations.

1. Introduction

Gobbinsite is a rare zeolite belonging to the gismondine group with ideal chemical formula between $Na_5(Al_5Si_{11}O_{32})\cdot11H_2O$ and $Na_4Ca(Al_6Si_{10}O_{32})\cdot11H_2O$, $Z = 1$ [1,2] and references therein, which can be found as late hydrothermal product in basalt cavities often in close association with phillippsite [3–7]. The other natural zeolites belonging to the gismondine group [8] are amicite [9] and garronite [10]. Like garronite, gobbinsite has a relatively high Si/Al ratio with a disordered framework cation distribution, and like amicite has Na as dominant extraframework cation. Many synthetic zeolites, among those MAPO-43 [11], SAPO-43 [12] and zeolites-P [13–17], share the GIS framework-type and Na–P2, in particular, is the synthetic counterpart of gobbinsite [14].

The GIS topological symmetry is $I4_1/amd$, with idealized unit-cell parameters $a = 9.8$ Å and $c = 10.2$ Å [18], which is reduced by framework distortions, tetrahedral cation ordering and extraframework site distribution [2]. This makes the GIS framework extremely "flexible", as shown by the large range of (real) space groups found for isotypic zeolites in order to accommodate the different chemical nature of framework and extraframework population. The GIS net is built by two intersecting sets of edge-sharing four-membered rings (hereafter: 4 mRs) chains [the so-called "double crankshaft" chains (Fig. 1)], stacked in order to give a three-dimensional network (Figs. 2 and 3). Two intersecting 8-membered rings (8 mR) channels run along the same chain directions (i.e. [100] and [010] in gobbinsite) (Figs. 2 and 3). An alternative way to describe this framework is through the so-called *gis*-cage composite building unit [18] (Fig. 4). Gobbinsite structure was first refined by Rietveld method [5,19] due to the paucity of single crystals. Later, the finding of a millimetric sample from Bundoora (Victoria, Australia) allowed Gatta et al. [6] to refine the crystal structure from single-crystal X-ray diffraction data (space group: *Pmnb* with $a \sim 10.09$, $b \sim 9.77$, and $c \sim 10.14$ Å). The refinement showed that Na (i.e. the dominant extraframework cation) fills the *gis*-cage in a partially occupied site near the channels intersections, whereas Ca partially occupies a site mutually exclusive with that of Na (Fig. 4). H_2O molecules lie in several partially occupied sites on the mirror plane perpendicular to [100], at the center of the 8 mR channel parallel to [010] (hereafter: 8 mR [010]) (Fig. 4).

Zeolites with GIS topology show a wide range of industrial applications. In this light, the crystal chemistry of the GIS-type compounds has been extensively investigated. Zeolites-P, in particular, are often used as detergent builders [20], can be easily synthesized from waste materials as coal fly ashes [21] or from low-grade natural zeolites [22,23] and have a high exchange

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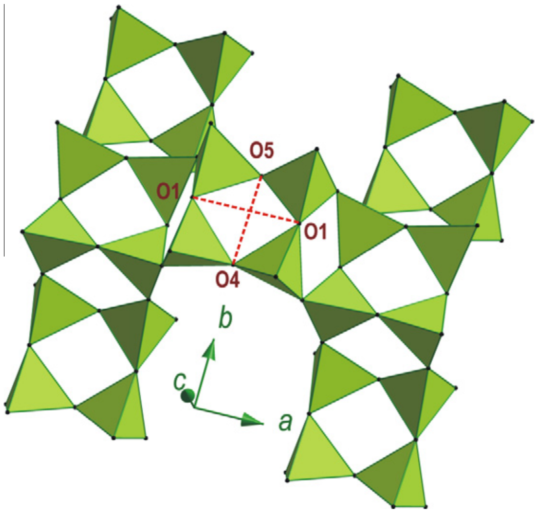

Fig. 1. The two sets of intersecting "double crankshaft" chains running along the *a* and *b* crystallographic axes of the gobbinsite framework, respectively. The 4 mR [0 0 1] diameters are shown.

capacity for many cations [24–26] and for ammonia [23] and cyanide [27]. However, compared with the ion exchange studies, investigation of the high-pressure/high-temperature behavior of materials with this "flexible" framework is less known. The high-pressure (H*P*) behavior of a natural gismondine was studied using both "non-penetrating" (i.e. silicon oil) [28] and "penetrating" (methanol:ethanol:water = 16:3:1) [29] *P*-transmitting fluids. In the latter case, a *P*-induced overhydration (PIH) of existing partially occupied sites was observed at a very low pressure, along with slightly different elastic behavior and structure evolution with respect to gismondine compressed in a non-penetrating medium. On the whole, both experiments revealed very low compressibilities for an open-framework material [30,31] and framework deformation mechanisms similar to that induced by dehydration under vacuum [32]. Lee et al. [33] and Jang et al. [34] studied the H*P* behavior of two synthetic analogues with GIS topology, both compressed in penetrating media: a K-gallosilicate (K-GaSi-GIS) and a K-aluminogermanate (K-AlGe-GIS), respectively. K-GaSi-GIS showed an early PIH and a change of compressional behavior due to a *P*-induced disordering of the extraframework constituents, whereas a linear unit-cell volume compression over the entire *P*-range investigated was shown by K-AlGe-GIS. Compressibility is also different, being higher in K-AlGe-GIS, and it is, in turn, differ-

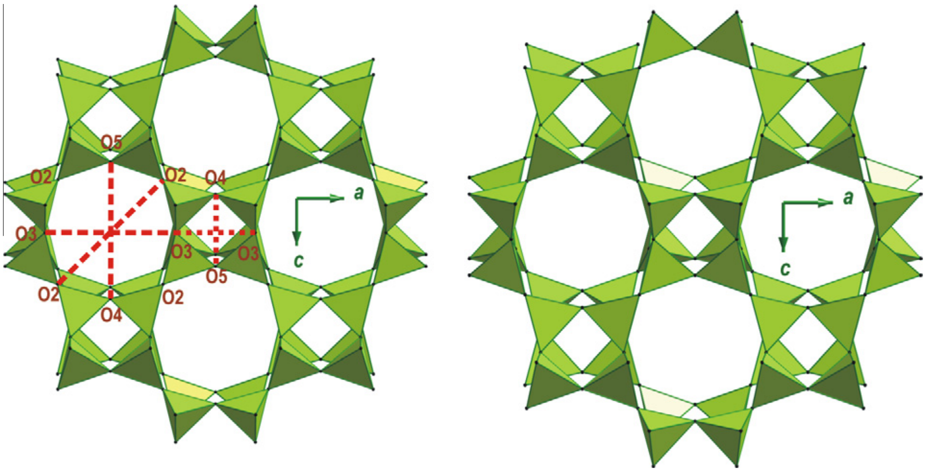

Fig. 2. The gobbinsite framework viewed down [0 1 0] at room pressure (*left*) and at 4.3 GPa (*right*). The 8 mR [0 1 0] and the 4 mR [0 1 0] diameters are shown.

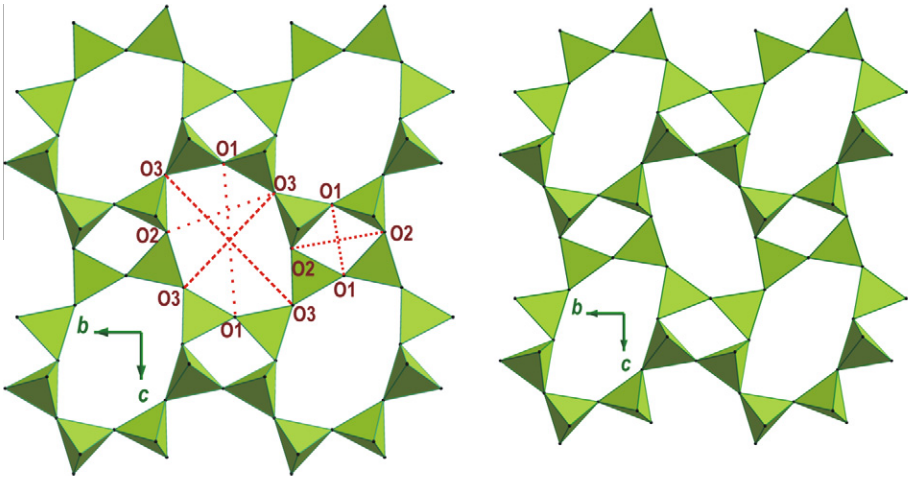

Fig. 3. The gobbinsite framework viewed down [1 0 0] at room conditions (*left*) and at 4.3(1) GPa (*right*), showing the distortion and the increase of ellipticity of the 8 mR [1 0 0] channels.